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Remote doping of graphene on SiO_2 with 5 keV x-rays in air

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I. INTRODUCTION

Due to its special band structure, certain electronic properties of graphene such as the resistivity are sensitive to electric fields perpendicular to the graphene layer.[1] Here, we report on the observation of changes in resistivity and charge carrier density of graphene on SiO_2/Si upon x-ray irradiation under ambient conditions. With a metal oxide semiconductor (MOS) structure, where graphene takes the role of the metal top gate, the effect is shown to be due to positive charge in the oxide (remote doping). The creation of such charged defects has been described theoretically[2] and has been studied experimentally[3,4] for applications in, e.g., dosimetry.[5] The effect of graphene resistivity change upon remote doping has been recently reported in graphene field effect transistors (GFETs) under UHV conditions.[6]

II. EXPERIMENT

We used commercially available monolayer graphene epitaxially grown on copper substrates.[7] It was transferred onto SiO_2/Si wafers with an oxide thickness of 93 nm via an electrochemical delamination method.[8] The graphene was contacted via four sputter-coated chromium/palladium contacts with 25 nm thickness per material. The contacts were arranged in a cross shape, allowing for both four-point resistance as well as for Hall effect measurements. Additionally, the silicon backside was contacted for capacitance measurements. See Figs. 1(a) and 1(b) for a sketch of the device and a light microscope image of the final sample's front side, respectively. An ^{55}Fe source with an activity of 1.3 GBq provided 5 keV x-rays.[9] For the given distance between source and sample the fluence was $\approx 2 \times 10^7$ photons $s^{-1} cm^{-2}$. All measurements were made inside a clean room[10] at ambient conditions. The capacitance measurements were made with an LCR measuring bridge; produced by Hameg Instruments, model H8118; using one of the front contacts and the back silicon contact. All Hall measurements were taken in fields of ± 1 T applied perpendicular to the basal plane of graphene. We studied one graphene gate which exhibited n-type carriers and one which exhibited p-type carriers.

III. THEORETICAL BACKGROUND

In MOS structures, measurements of the capacitance C(V) across the oxide can be used to determine the doping level of the semiconductor (p- or n-type) and the charge within the oxide layer from the shift of the flat band voltage ΔV_{FB}.[11] The additional charge Q inside the oxide of the MOS structure can be calculated as

$$Q = \Delta V_{FB} C_{Ox}, \tag{1}$$

for a given capacitance C_{Ox} of the oxide layer. This is a useful way to measure the charge induced in the oxide by irradiation.

In order to study the effects of the charges in the oxide on the graphene placed on top of the oxide, four point resistance measurements following the Van-der-Pauw method[12,13] as well as Hall effect measurements were performed before, during and after the irradiation. This allowed to determine sheet resistance, charge carrier density, and mobility.[14] The carrier density n is calculated from the Hall coefficient R_H as

$$n = (R_H e)^{-1}, \tag{2}$$

with e the electron charge. The sign of the charge carrier density corresponds to the type of charge carriers, i.e., electrons or holes.[14] The mobility of the charge carriers μ is calculated as

$$\mu = (R_\square n e)^{-1}, \tag{3}$$

with $R_\square$ the sheet resistance of the graphene. In graphene, the charge carrier type is determined by the location of the Fermi level with respect to the Dirac energy, where the apices of the Dirac cones lie; see Fig. 2(c).

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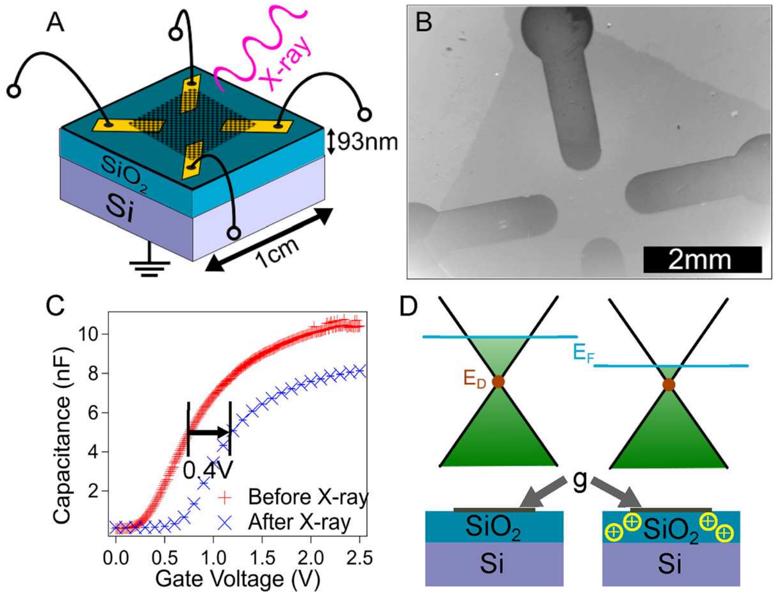

FIG. 1. (Color online) (a) Schematic of a MOS device with top contacts indicated in yellow and the graphene gate shaded. (b) Light microscopy image of the sample front after sputtering with a cross-shaped mask showing the dark graphene on top of the oxide as well as the darker contacts. (c) Measurements of the capacitance across the oxide of the n-Si device as a function of gate voltage before and after irradiation for 2.2 h showing the shift in flat band voltage due to positive charge accumulation in the oxide layer. (d) Sketch of the graphene band structure near the K points showing Dirac cones and energies E_D. The effect of positive charges in the oxide on the Fermi level of the graphene is shown on the right. The Fermi level shift reflects the shift in flat band potential.

A schematic illustration of the effect of oxide charges on n-type graphene is shown in Fig. 1(d).

IV. RESULTS AND DISCUSSION

A. Capacitance measurements

Measurements of C(V) curves of an n-type semiconductor device before and after 22 h irradiation is shown in 1 C. The C(V) characteristics shifts by (0.4 ± 0.1) V and the saturation capacitance decreases. From operando measurements of the capacitance at a gate voltage of 0.6 V we confirm that the shift occurs only upon irradiation. The shift corresponds to a change in charge density of $1.5 \times 10^{-4}\,\mathrm{C\,m^{-2}}$ assuming a uniform charge distribution in the oxide; as expected, the induced charges are positive. Knowing the dielectric constant of SiO_2, the thickness of the oxide layer and having measured the saturation capacitance before irradiation (for $V > 2$ V) we determine a gate area of $27\,\mathrm{mm}^2$ or an average distance of about $1\,\mu$m between single charges after irradiation.

B. Measurement of transport properties

1. n-type graphene

For the n-type graphene sample, we observe an increase in sheet resistance from (3846 ± 2) to $(6568.9 \pm 0.5)\,\Omega$ upon x-ray irradiation for 22 h. This is accompanied by a decrease in Hall charge carrier density from $-(8.1 \pm 0.2) \times 10^{13}$ to $-(5.03 \pm 0.03) \times 10^{13}\,\mathrm{cm}^{-2}$ [red symbols Fig. 2(b)]. Therefore, positive charges in the oxide shift the Fermi level of the graphene toward the Dirac point, decrease the density of states at the Fermi level and thus also the conductivity [see Fig. 2(c)]. The charge carrier mobility remains close to constant, changing from (20 ± 1) to (18.8 ± 0.3) $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$, indicating that the radiation does not deteriorate the graphene gate. This data are shown in Fig. 2(b) for both types of graphene gates.

2. p-type graphene

The conductivity measured for a p-type graphene sample on p-Si during irradiation is shown in Fig. 2(a). During this irradiation, several Hall effect and capacitance measurements were performed as shown in Fig. 2(b) [blue symbols]. Over the entire duration of the experiment, the charge carrier density changes from $(2.56 \pm 0.04) \times 10^{13}$ to $(3.021 \pm 0.006) \times 10^{13}\,\mathrm{cm}^{-2}$ while the charge carrier mobility again decreases only slightly from $-(102.0 \pm 0.5)$ to $-(95.6 \pm 0.6)\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. Overall, the sheet resistance decreases from (2802.0 ± 0.4) to $(2556.0 \pm 0.4)\,\Omega$. This is consistent with the influence of positive charges in the oxide support on p-type graphene as shown in Fig. 2(c).

At room temperature, the change in resistance remains stable for more than 24 h after the end of the irradiation, showing no sign of a return to the original state. However, heating the sample to 200 °C for 14 h restores the sheet resistance to $(2379.8 \pm 0.5)\,\Omega$, a value close to the value before irradiation.

In the p-type sample, the irradiation affected the graphene much more slowly. This is likely an effect of the voltage applied across the n-type sample's oxide to measure the capacitance shift. Such a voltage may lead to a quicker accumulation of holes close to the g/SiO_2 interface.[15]

V. CONCLUSIONS

We observed effects of remote doping on graphene in ambient condition. The x-ray irradiation of a g/SiO_2/Si

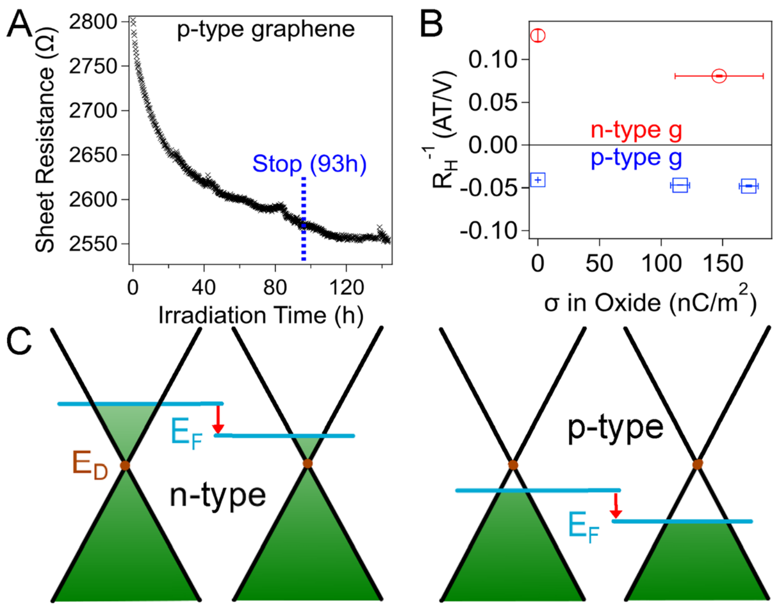

FIG. 2. (Color online) (a) Sheet resistance as function of irradiation time for p-type graphene. The irradiation was stopped after 93 h. The resistance continues to drop after this time before it levels out and remains stable for several hours as observed with GFETs (Ref. 6). (b) Inverse Hall coefficient R_H^{-1} as a function of oxide charge density for both samples. (c) Diagram showing the shift in Fermi energy in graphene with n- or p-type carriers as they are caused by positive charges in the oxide. The density of states at the Fermi level increases for p-type carriers while it decreases for n-type carriers.

system induces positive charges in the oxide layer. With Hall effect and resistance measurements of the graphene, we have observed effects consistent with positive charges in the oxide that affect the graphene transport properties in both p-type and n-type graphene samples. The charges in the oxide appear to be stable under ambient conditions for several hours but can be neutralized by heating the device. The reported effect where a space charge in the insulating support quickly and strongly affects the charge carrier concentration in graphene under ambient conditions may become useful in devices like x-ray dosimeters or where graphene shall be adjusted to a given doping level.

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